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[54] Rubber composition for tire treads

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Specification

1. Title of Invention

Rubber composition for tire treads.

2. Scope of Patent Claim

A rubber composition for tire treads in which 40-70 weight parts of carbon black which satisfy the requisites of nitrogen adsorption specific surface area (N_2SA) of 105~125 m^2/g, compressed DBP oil absorption amount (24M4DBP) of 85~100 ml/100 g and comparative tint which satisfies the following equation

$$\text{Tint} > 145 - 31.5\ (24M4DBP/N_2SA)$$

are blended in 100 weight parts of blended rubber which consists of 10-60 weight parts of polybutadiene rubber with a trans 1,4-bond content of 70% or more and 90-40 weight parts of at least one type of rubber selected from the group comprising natural rubber, polyisobutadiene rubber and styrene-butadiene copolymer rubber with a styrene content of 15 wt% or more.

3. Detailed Description of the Invention

[Technical Field of Invention]

This invention relates to a rubber composition for tire treads, specifically, a rubber composition in which the wear resistance and resistance to cutting-chipping are improved without sacrificing the heating characteristics and braking performance to provide a tire which is especially desirable as the rubber for the treads of large tires used in trucks and buses.

[Conventional Techniques]

The demand for rubber material having great braking performance at low heating as well as outstanding wear resistance for application to the tread of automobiles has intensified in recent years accompanying the expansion of high-speed highways and enhanced vehicle performance.

However, while the proportion of use of large tires for trucks and buses on good roads and high-speed highways has been increasing, there are still more cases in which such tires are used on poor roads, as before, than are tires for passenger cars. Since tires for dump trucks and other off-the-road vehicles are used on extremely poor roads, such as mountain roads and gravel roads, problems involving cutting and chipping as well as heating and wear characteristics cannot be ignored.

Thus, great improvement of the wear resistance for high-speed applications while improving rather than sacrificing the resistance to cutting and chipping for applications on poor roads are required in the case of these large tires.

However, blends of natural rubber and high cis-polybutadiene rubber primarily have been used in the past in the tread rubber of large tires.

Such blends are used because natural rubber has good heating characteristics and resistance to cutting and chipping but inferior wear resistance, while high cis-polybutadiene rubber is effective in improving the wear resistance while suffering from inferior resistance to cutting and chipping.

Furthermore, the method of blending carbon black with small particle size and great reinforcing properties has been used to improve the wear resistance.

However, deterioration of the resistance to cutting and chipping cannot be avoided in blends of high cis-polybutadiene rubber using these methods. On the other hand, deterioration of the working properties and increase of the heating properties are induced when using carbon black with small particle size, and rubber material which adequately satisfies the higher performance requirements which have been imposed recently has not been provided to date.

[Object of Invention]

The object of this invention is to provide a rubber composition which can be used ideally in the tread of large tires, especially in trucks and buses, in which the wear resistance and resistance to cutting and chipping are improved without sacrificing the heating characteristics and braking performance.

[Structure of Invention]

The rubber composition for tire treads pursuant to this invention to obtain the aforementioned objects has 40~70 weight parts of carbon black which satisfy the requisites of nitrogen adsorption specific surface area (N_2SA) of 105~125 m^2/g, compressed DBP oil absorption amount (24M4DBP) of 85~100 ml/100 g and comparative tint which satisfies the following equation

$$\text{Tint} > 145 - 31.5\ (24M4DBP/N_2SA)$$

blended in 100 weight parts of blended rubber which consists of 10~60 weight parts of polybutadiene rubber with a trans 1,4-bond content of 70% or more and 90~40 weight parts of at least one type of rubber selected from the group comprising natural rubber, polyisobutadiene rubber and styrene-butadiene copolymer rubber with a styrene content of 15 wt% or more.

The rubber component used in this invention is blended rubber comprising 10~60 weight parts of polybutadiene rubber with a trans 1,4-bond content of 70% or more, preferably a content of 75~90%, and 90~40 weight parts of at least one type of rubber selected from the group comprising natural rubber, polyisobutadiene rubber and styrene-butadiene copolymer rubber with a styrene content of 15 wt% or more.

Polybutadiene rubber is produced by solution polymerization. For example, high trans-polybutadiene rubber which can be used in this invention can be produced by using a compound catalyst consisting of barium compounds and organic lithium compounds.

It is difficult to produce rubber in which the trans 1,4-bond content is 70% or more since the microstructure of the butadiene section of polybutadiene rubber obtained by emulsion polymerization cannot be altered. Furthermore, among the physical characteristics, the heating properties are inferior.

The improvement in the resistance to cutting and chipping would be inadequate if the trans 1,4-bond content is less than 70%, while the tensile strength, the tearing resistance and the wear resistance are improved if the trans 1,4-bond content should exceed 70%, but the effects of raising the hardness are especially outstanding and the resistance to cutting and chipping are greatly improved.

Furthermore, the proportion of use of high cis-polybutadiene rubber in blended rubber is usually in the range of 10~60 weight parts, preferably 15~50 weight parts. There is little improvement in the wear resistance and resistance to cutting if less than 10 weight parts are used, while the resistance to chipping declines if more than 60 weight parts are used.

The rubber which is blended with high cis-polybutadiene rubber would be at least one type of rubber selected from the group comprising natural rubber, polyisobutadiene rubber and styrene-butadiene copolymer rubber with a styrene content of 15 wt% or more, as mentioned above. Natural rubber and polybutadiene rubber would be especially desirable in terms of the heating properties.

The carbon black used in this invention must satisfy the requisites of nitrogen adsorption specific surface area (N_2SA) of 105~125 m^2/g, compressed DBP oil absorption amount (24M4DBP) of 85~100 ml/100 g and comparative tint which satisfies equation (1) below

$$\text{Tint} > 145 - 31.5\ (24\text{M4DBP}/N_2SA) \qquad (1)$$

Carbon black which does not satisfy these conditions, for example, carbon black in which the nitrogen adsorption specific surface area is less than 105 m^2/g, does not provide adequate wear resistance. Conversely, carbon black in which the specific surface area exceeds 125 m^2/g is undesirable since the heating characteristics deteriorate.

Furthermore, the resistance to cutting and the wear resistance decline if the compressed DBP oil absorption amount is less than 85~100 ml/100 g, while the tensile stress increases and the resistance to chipping deteriorate, which are undesirable, if the amount exceeds 100 ml/100 g.

It is important that the carbon black used in this invention satisfy aforementioned equation (1).

The nitrogen adsorption specific surface area (N_2SA) represents the surface area (m^2) per unit weight of carbon black (g) computed from the BET formula due to adsorption of nitrogen gas on the surface of carbon black particles. It virtually corresponds to the size of the carbon black particles.

The compressed DBP oil absorption amount (24M4DBP) represents the amount of DBP (dibutyl phthalate) absorption measured after compression of carbon black four times under pressure of 24,000 psi. This is a method of measuring virtually the true structure of carbon black in the state of kneading in rubber.

Furthermore, the comparative tint represents the brightness of the color when carbon black has been kneaded in a vehicle with white pigment followed by application onto a glass plate. It is represented as an index when contrasted with the standard product.

More concentrated colors are represented by greater comparative tint values.

The results of detailed examinations by the inventors of the comparative tint of carbon black revealed that the comparative tint is determined in virtually all conventional hard carbon black by the nitrogen adsorption specific surface area (N_2SA), which represents the particle size, and by the compressed DBP oil absorption amount (24M4DBP), which represents the structure. The fact is obvious that the following relation applies between these two.

$$135\text{-}31.5\ (24\text{M4DBP}/N_2SA) < \text{Tint} < 145 - 31.5\ (24\text{M4DBP}/N_2SA)$$

However, it is difficult to greatly improve both the wear resistance and the resistance to cutting and chipping of carbon black in this range.

Thus, the results of continued examination indicated that the carbon black in which the comparative tint satisfies Tint > 145 - 31.5 (24M4DBP/N_2SA) is effective in markedly improving the wear resistance and the resistance to cutting and chipping without altering other characteristics. Moreover, the fact was discovered that the effects were especially great in the aforementioned blended rubber system. The fact was confirmed that this is an indispensable requisite for this invention.

The amount of such carbon black which is used should be 40~70 weight parts per 100 weight parts of blended rubber, preferably 40~60 weight parts. Adequate reinforcing characteristics are not attained if less than 40 weight parts are used, and the wear resistance as well as the resistance to cutting are markedly reduced.

Furthermore, the wear resistance is improved if more than 70 weight parts are used, but the heating becomes excessive and the resistance to chipping declines, both of which are undesirable.

[Effects f Invention]

As indicated above, this invention concerns a rubber composition for tire treads in which 40-70 weight parts of carbon black which satisfy the requisites of nitrogen adsorption specific surface area (N_2SA) of 105-125 m^2/g, compressed DBP oil absorption amount (24M4DBP) of 85-100 ml/100 g and comparative tint which satisfies the following equation

$$\text{Tint} > 145 - 31.5\ (24M4DBP/N_2SA)$$

are blended in 100 weight parts of blended rubber which consists of 10-60 weight parts of polybutadiene rubber with a trans 1,4-bond content of 70% or more and 90-40 weight parts of at least one type of rubber selected from the group comprising natural rubber, polyisobutadiene rubber and styrene-butadiene copolymer rubber with a styrene content of 15 wt% or more. As a result, the rubber composition has improved wear resistance and resistance to cutting and chipping without sacrificing the heating characteristics and braking performance.

This rubber composition can be used especially in large tires for trucks and buses.

Example of this invention are explained below.

[Examples]

The characteristics of the polybutadiene rubber and carbon black used in the examples are illustrated in Tables 1 and 2.

The polybutadiene rubber, carbon black and other compounds which are incorporated are kneaded using a Bumbury's mixer and open roll based on the following blending formula to produce the rubber composition.

The rubber composition was vulcanized for 20 minutes at 160°C to complete preparation of the individual test specimens for use as the examples and comparative examples of this invention.

Tables 3 and 4 below present the results of evaluating the rubber compositions in these examples and comparative examples.

The details of the rubber and carbon black are presented in Tables 3 and 4.

(Blending formula)

Component	Weight parts
rubber	100.0
carbon black	variable
zinc white	3.0
stearic acid	1.5
acrylonitrile	5.0
vulcanization accelerator CBS *	1.0
sulfur	1.75

*) N-cyclohexyl-2-benzothiazyl sulfenamide

Furthermore, the method of evaluating the rubber composition of this invention is presented below.

(Heating characteristics).. This conformed to JIS K6301. The Ryubukke* resilience elasticity value at 60°C was used.

(Braking performance).. The wet skid resistance values based on the British portable skid test were compared by indices.

The road surface was a safety walk produced by 3M Co.. The pavement was moistened with distilled water and measured at room temperature.

(Wear resistance).. This was measured at 60 rpm under a load of 4.5 kg using a pico abrasion tester pursuant to ASTM D2228. The index was represented by the reciprocal of the amount of abrasion decrease.

The wear resistance improves as the value increases.

(Resistance to cutting).. A load of 7 kg was imposed on a needle tilted at a 45 degree angle which was dropped from an elevation of 15 cm onto vulcanized rubber 4 cm thick. The depth of the scar which had been produced was determined, and the reciprocal is represented by an index.

The resistance to cutting improves as the value becomes larger.

(Resistance to chipping).. A test device in which the Modified Lambourn Dunlop Machine was improved to a new model was applied to RAPRA 6T103-9522, and miniatures having 68ϕ × 26 m/m lap grooves were used as samples. A disk with two projections was tested 10,000 times under a 35 kg load. The weight decrease due to chipping was measured, and the reciprocal is represented by an index.

The resistance to chipping improves as the value becomes greater.

Examples 1, 2 and Comparative Examples 1-5

The rubber composition of this invention exhibits greatly improved wear resistance and resistance to cutting without any decline in the heating characteristics and the braking performance, as illustrated in Table 3.

The improvement in the wear resistance and the resistance to cutting are especially great.

Examples 1, 3, 4 and Comparative Examples 1, 6-12

Table 4 illustrates the effects of modifying the carbon black used in Example 1.

The properties do not decline when carbon black which does not satisfy aforementioned equation (1) is used, as illustrated in Comparative Example 6, but the objects of this invention are not obtained with adequate improvement.

On the other hand, carbon black used in this example exhibits great improvement in the wear resistance and the resistance to cutting and chipping.

*Tr. note. Phonetic transliteration

Table 1

Type of polybutadiene rubber		(*2) BR-1	BR-2	BR-3
Polymerization method		Solution polymerization	Emulsion polymerization	Solution polymerization
Microstructure of butadiene section (*1)	Cis (%)	98	12	19
	Trans (%)	1	68.5	75.6
	Vinyl (%)	1	19.5	5.4

(*1) Measured using an infrared spectrophotometer
(*2) Nipol 1220 (product of Nihon Zeon Co., Ltd.)

Table 2

Type of carbon black	CB-1	CB-2	CB-3	CB-4	CB-5	CB-6	CB-7	CB-8
N_2SA (*3) (m^2/g)	116	79	143	106	123	122	110	114
24 M4DBP (*4) (ml/100 g)	96	90	100	71	103	92	95	99
Tint (*5)	115	101	120	115	118	124	122	121
145-31.5 (24 M4DBP/N_2SA)	119	109	123	124	119	121	118	118

(*3) Attributable to ASTM D 3037
(*4) attributable to ASTM D 3493
(*5) IRB #3 is taken as 100 according to JIS K 6221

Table 3

		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Example 1	Comp. Ex. 4	Example 2	Comp. Ex. 5
Rubber	Natural rubber	80	80	80	80	70	70	20
	BR-1	20	20			30		
	BR-2			20				
	BR-3				20		30	80
Carbon black	CB-1	50						
	CB-7		50	50	50	50	50	50
Resilience elasticity (%) 60°C		62	61	58	62	62	62	61
Wet skid resistance (index)		100	100	107	105	97	103	89
Wear resistance (index)		100	103	99	112	105	119	243
Resistance to cutting (index)		100	101	103	106	100	108	115
Resistance to chipping (index)		100	100	102	103	92	102	93

Table 4

		Comp. Ex. 1	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10	Example 3	Example 1	Example 4	Comp. Ex. 11	Comp. Ex. 12
Rubber	Natural rubber	80	80	80	80	80	80	80	80	80	80	80
	BR-1	20										
	BR-3		20	20	20	20	20	20	20	20	20	20
Carbon black	CB-1	50	50									
	CB-2			50								
	CB-3				50							
	CB-4					50						
	CB-5						50					
	CB-6							50				
	CB-7								50		35	75
	CB-8									50		
Resilience elasticity (%) 60°C		62	61	67	59	61	60	60	62	61	67	53
Wet skid resistance (index)		100	102	99	104	98	103	103	105	102	100	108
Wear resistance (index)		100	103	86	105	84	107	110	112	115	65	207
Resistance to cutting (index)		100	103	98	102	94	104	104	106	107	92	116
Resistance to chipping (index)		100	101	102	101	107	96	105	103	103	110	93